THE RUTHENIUM(VIII)-CATALYZED OXIDATION OF ILLINOIS NO. 6 BITUMINOUS COAL. AN APPLICATION OF GC-FTIR SPECTROSCOPY FOR STRUCTURAL ANALYSIS.

Leon M. Stock and Shih-Hsien Wang

Department of Chemistry, University of Chicago, Chicago, IL 60637 USA

INTRODUCTION

Sharpless and his coworkers pointed out that ruthenium tetroxide could be used very effectively for the oxidation of aromatic compounds in the presence of acetonitrile (1). For example, 4-(1-pentyl)biphenyl is converted almost quantitatively to a mixture of hexanoic acid, benzoic acid and 4-pentylbenzoic acid. This reagent has been used successfully for the oxidation of Illinois No. 6 coal and the quantities of many aliphatic and aromatic mono-, di-, tri-, and tetracarboxylic acids have been determined for several different coals (2-5). Mass spectroscopy has been used almost exclusively in these studies. In related work, Mallya and Zingaro (6) investigated the ruthenium ion-catalyzed oxidation of Texas lignite using infrared spectroscopy. They pointed out that the stretching bands of the carbon-carbon bonds of the aromatic ring at 1600 cm^{-1} decreased and a new carbonyl band at 1700 cm^{-1} appeared. Their work and other factors prompted us to consider the utilization of GC-FTIR spectroscopy for the further analysis of the product distribution obtained in the oxidation of Illinois No. 6 coal.

EXPERIMENTAL PART

Coal Sample.--Illinois No. 6 coal [77.2%C, 5.6%H, 0.68%N, 0.15%Cl, 2.95% organic S, 0.89% pyritic S, 0.00% sulfate, and 12.5% O (by difference)] was obtained from the Peabody mine in Pawnee, Illinois. The sample was extracted before oxidation with aqueous hydrochloric acid, aqueous sodium hydroxide, benzene-methanol, and chloroform as described by Hayatsu and coworkers (7).

Oxidation Procedure.--The oxidation reactions were carried out as described previously (3,4,5) using coal (400 mg), ruthenium(III) chloride trihydrate (12 mg), and sodium periodate (4g) in a mixture of carbon tetrachloride (8 ml), acetonitrile (8 ml) and water (12 ml). The mixture was stirred for about 24 hours at room temperature. The solids were separated by filtration and the organic and the aqueous phases were retained. The mildly acidic aqueous layer was washed with four portions of ether (15 ml). The solid was also washed with ether. All the organic extracts were combined and dried with sodium sulfate. The solvents were removed with a rotary evaporator at 40°C. The acids in the concentrated solution were methylated using 0.35M diazomethane in ether (10 ml). The ether was carefully removed using a rotary evaporator at room temperature. This procedure was repeated three times and the final solution was examined by gas chromatography-Fourier transform infrared spectrometry and mass spectrometry.

Gas Chromatography-Fourier Transform Infrared Spectrometry.--An HP Model 5890 gas chromatograph and a Nicolet Model 60SX Fourier Transform Infrared Spectrometer were used in this study. The chromatograph was equipped with a 0.53mm X 25 meter, OV-1701 megabore column supplied by J & W Scientific, Inc.

Typical conditions for the analysis are noted: injection port, 250°C; the oven temperature was programmed to hold at 50°C for one minute then to heat to 270°C at the rate of 4°C/min and then to hold at 270°C. For all the spectra, 4 scans measured at 4 cm^{-1} resolution were co-added.

Gas Chromatography-Mass pectrometry.--The GC-MS results were obtained using an HP Model 5790A gas chromatograph with a VG Model 70-250 mass spectrometer. The chromatograph was equipped with a 50 meter, OV-1701 (0.25μ) capillary column supplied by Quadrex Corporation, Inc. The conditions for the analysis are noted: injection port, 250°C; the oven temperature was programmed to hold at 50°C for one minute then to heat to 270°C at the rate of 7°C/min and then to hold at 270°C. One scan per second was recorded in these low resolution, electron impact mass spectral analyses.

RESULTS AND DISCUSSION

The ruthenium(VIII) ion-catalyzed oxidation reaction of Illinois No. 6 bituminous coal produces a large array of different carboxylic acids. These acids were quantitatively converted to the corresponding methyl esters by repetitive esterification reactions with diazomethane. The GC-FTIR chromatograms obtained using conventional capillary columns were not entirely suitable. However, the separations obtained using megabore capillary columns were more than satisfactory and suitable infrared spectra could be recorded for most of the reaction products. Chromatographic procedures were developed to enable facile comparison of the mass and infrared spectra.

Many aliphatic di-, tri-, and tetracarboxylic acids as well as the benzenedi-, tri-, tetra-, and pentacarboxylic acids can be readily detected and identified by GC-MS procedures (4,5). However, certain of the products cannot be unambiguously identified by MS tactics alone. We were particularly concerned that certain hydroxyacids and lactones might have escaped detection.

Inasmuch as sharp oxygen-hydrogen stretching frequencies are readily observed in the vapor phase, the infrared spectra were systematically scanned for the appearance of this absorption. Only three compounds among the host of reaction products exhibited this absorption. Inasmuch as these substances are produced only in trace amounts, this finding confirms the previous conclusion that aromatic hydroxylic compounds such as naphthol are oxidized to benzenedicarboxylic acid and that aliphatic hydroxylic compounds are degraded to simple aliphatic mono-, di-, and tricarboxylic acids. The absence of significant amounts of hydroxy compounds in the reaction product is in accord with the observations of Sharpless and coworkers (1) who reported that 3-phenyl-1,2-butanediol is oxidized to 2-phenylpropanoic acid under the experimental conditions, equation (1).

$$C_6H_5CH(CH_3)CHOHCH_2OH \xrightarrow{92\%} C_6H_5CH(CH_3)CO_2H \qquad (1)$$

The position of the carbon-oxygen double bond stretching frequency is very dependent upon its structural environment with significant differences in the absorption frequencies of aromatic and aliphatic esters, lactones, anhydrides and so forth. The carbonyl stretching frequencies of the methyl esters of aliphatic acids, for example, dimethyl butane-1,4-dioate, appear near 1760 cm^{-1}, whereas the corresponding frequencies of methyl benzenecarboxylates, for example, trimethyl benzene-1,2,3-trioate, appear near 1750 cm^{-1}. The carbonyl frequencies were examined to establish that proper structural assignments had been made in the previous work. No discrepencies were uncovered. However, several new compounds were detected. The carbonyl frequencies for these rather non-abundant compounds, not more than 1% of the abundance of dimethyl butane-1,4-dioate are listed in Table 1.

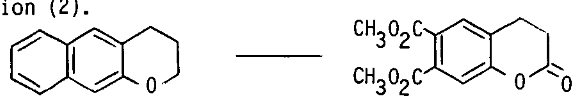
Table 1. The carbonyl bands of several novel substances in the oxidation of Illinois No. 6 coal

Compound	Frequency and Intensity
1	1720 (vs), 1704 (vs)
2	1820 (s), 1755 (s)
3	1824 (m), 1758 (vs)
4	1806 (m), 1755 (vs)
5	1809 (m), 1754 (vs)
aliphatic ester	around 1760
aromatic ester	around 1751

Compound 1 is quite volatile and exhibits a very intense carbonyl absorption centered at 1710 cm^{-1}. The absence of significant intensity in the carbon-hydrogen stretching region indicates that the substance is not a methyl ester. Indeed, the infrared spectrum is reminiscent of butane-2,3-dione. Hence, we infer that this non-abundant substance may be a 1,2-diketone produced as a byproduct of the principal reaction sequence.

Compound 2 exhibits two broad, equally intense carbonyl absorptions at 1755 and 1820 cm^{-1}. These observations and the strong absorption at 742 cm^{-1} imply that this substance is an aryl anhydride derivative.

Compounds 3,4, and 5, which differ considerably in volatility, exhibit very similar carbonyl absorption frequencies. In each case, there are two relative sharp bands in the carbonyl region. The weaker band is centered between 1804 and 1809 cm^{-1} and the stronger band is centered between 1754 and 1758 cm^{-1}. These compounds all exhibit rather intense carbon-hydrogen absorptions. We postulate that these compounds are lactones with from one to three ester groups in the same molecule. These substances may form as illustrated in equation (2).



(2)

The abundance of lactones in the oxidation products of this bituminous coal appears to be much less than in the oxidation of Texas lignite (6).

CONCLUSION

Gas chromatography infrared spectroscopy provides useful information concerning the oxidation products of coals. The new data obtained by this technique confirm earlier conclusions concerning the low abundance of hydroxyl compounds among the oxidation and indicate that lactones are formed in low relative abundance during the oxidation of a bituminous coal.

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